The Determination of Mercury in Coal by Flameless Atomic Absorption

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Recently there has been considerable interest in the potential release of volatile mercury to the atmosphere from power plants. The mercury, naturally occurring in coal at very low levels, is volatilized during combustion of the coal in fossil fuel fired steam generating plants. The present consumption of coal (in excess of 300 million tons per year) could result in the release of a significant quantity of mercury to the atmosphere. This potential problem has resulted in the need for the development of analytical procedures for determining the mercury concentrations in coal.

The United States Bureau of Mines instigated a round-robin analytical program for mercury in coal with 12 independent laboratories in the Spring of 1971. Eleven coal samples, representing a cross-section of coals in this country, were furnished to each participant. Each participating laboratory developed its' own analytical method and submitted its' data to the Bureau of Mines at the completion of analyses. The methods and results presented in this paper represent our participation in this program.

Analytical procedures presently being utilized for mercury in coal determinations may be divided into four general catagories: (1) neutron activation, (2) amalgamation-flameless atomic absorption, (3) wet digestion-flameless atomic absorption, and (4) oxygen bomb combustion-flameless atomic absorption. All of these methods can produce accurate results although some are considerably more difficult than others. This paper presents an amalgamation-flameless atomic absorption procedure.

The cold vapor flameless atomic absorption procedure for mercury was developed for the analyses of water and other digestable materials such as fish, tissue, etc.[1] The material is digested in a strong acidic oxidizing media. This solution is then reduced and aerated, volatilizing the mercury which is carried by an air stream through a quartz cell located in the optical path of an atomic absorption spectrophotometer. Gold and silver amalgamation was added as an intermediate step to (1) increase sensitivity (preconcentrate the mercury after aeration) and (2) eliminate interferences from aromatic organic compounds, sulfide, and water vapor that also absorb at the 2536 A mercury line.[2] Coal, which is extremely difficult to wet digest, was not directly amenable to the above procedure. The method is adapted to mercury in coal analysis by firing the coal sample in a closed system, volatilizing the mercury which is separated from the other gaseous by-products and then analyzed by flameless atomic absorption. The mercury is isolated from the interferents by bubbling the volatiles through an acidic oxidizing solution in which the mercury is oxidized and subsequently absorbed into the solution. After the solution is reduced and aerated, an air stream carries the mercury through a silver or gold amalgamator which quantitatively adsorbs the mercury. The amalgam is then fired in an induction furnace, instantaneously revolatilizing the mercury which is carried through a quartz tube in the optical path of the spectrophotometer. The mercury absorption is recorded on a strip chart recorder as a very sharp peak with a sensitivity of 0.01 μg of mercury.

A schematic of the apparatus is shown in Figure 1. A Leco single or double induction furnace is used in conjunction with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. An air flow rate of 1.5 to 2.0 liters per minute is maintained through the system during the analysis. The combustion chamber (A) is constructed of quartz and is designed to hold a quartz enclosed graphite crucible. A picture of the oxidation chamber (A) is shown in Figure 2. A drying tube (E) is filled with magnesium perchlorate. The amalgamator (F) is constructed of ½ inch diameter quartz tubing and contains a porous plate that supports 6 - 8 grams of 0.007 inch thick gold or silver foil cut into approximately 1/16 inch square sections. The absorption cell is constructed of pyrex with quartz endplates.

A 500 mg coal sample is weighed in a quartz graphite crucible and positioned in the induction furnace (A). The air flow rate is adjusted and the sample is fired for 1½ minutes at the variac control setting of 60% and then fired an additional 30 seconds at a 75% setting. Initial firing of the sample at 75% will result in 'flashing' of the sample and a resultant plugging of the combustion chamber. Volatilized mercury and the other gaseous by-products are bubbled through the acidic oxidizing solution in the aeration chamber (B). The three-way stopcock (D) is opened to vent the non-absorbed combustion products. After the two minute firing period and collection of the mercury in the oxidizing solution, the excess oxidant and mercury are reduced by the addition of a reducing agent with a syringe through the septum cover (C). The solution is then aerated for two minutes collecting the revolatilized mercury on the gold or silver amalgamator (F). The induction furnace (F) is then fired, instantaneously releasing the mercury which is carried by the air stream through the quartz cell. The detachable tube containing the reduced oxidizing agent is replaced with fresh solution and the procedure is repeated for another coal sample. Approximately 5 minutes is required for each determination. Blank determinations must be routinely performed. Standards are obtained by replacing the oxidizing solution with known mercury in water samples and repeating the above procedure deleting the combustion step.

Preliminary investigations included studying ICl, $KMnO_4$-H_2SO_4, and $KMnO_4$-HNO_3 as possible oxidizing solutions. Mercury would not amalgamate when aerated from ICl solutions, possibly due to some interference from I_2 which is also released. Some stability and equilibrium problems were observed with $KMnO_4$ - H_2SO_4 solutions. $KMnO_4$-HNO_3 provided a stable oxidizing solution and was used to obtain the reported data. The solution is prepared by adding 5 ml of concentrated HNO_3 to 25 ml of a filtered 6% $KMnO_4$ solution which is then diluted to 50 ml with distilled water for each analysis. The blank determinations are made on these solutions. A considerable excess of permanaganate must be present in the tubes since the SO_2 released from the coal in the combustion process will also reduce the permanganate. These solutions are prepared in mass and are stored immediately prior to the beginning of a series of analyses. After the volatilized mercury is collected in the oxidizing solution the excess permanganate is reduced with 5 ml of a 10% hydroxylamine hydrochloride solution and the mercury is then reduced with 1 ml of 20% $SnCl_2$ in 50% HCl. Both of these reducing agents are added by syringe through the septum cover.

The 1.5 to 2.0 liter per minute air flow rate is a compromise between the optimum flow rates for greatest sensitivity, quickest cooling of the quartz-graphite crucible after firing, and fastest aeration (revolatilization of all the mercury) of the reduced oxidizing solution. Compressed air was found to be adequate, eliminating the necessity of using oxygen. Gold and silver foil both worked very well in the amalgamator but the silver foil did require daily cleaning.

The coal samples were air dried. The samples furnished by the United States Bureau of Mines were received crushed to minus 60 mesh, the Illinois Geological Survey samples were crushed to minus 20 mesh and the Tennessee Valley Authority samples were run as sampled from the Muscle Shoals' Colbert Steam Generating Plant. The TVA samples include three fly ash samples. The results of the analyses are presented in Table 1. The total sulfur and pyritic sulfur values were furnished by the Bureau of Mines and the Illinois Geological Survey. The sulfur concentrations were determined from moisture free samples. This data is included because of the suggested concentration of the mercury in the pyritic fraction of the coal.[3]

Table 1. Results of analyses of mercury in coal.

Sample No.	DRB-A	DRB-B	DRB-C	DRB-D	DRB-E
State	Ohio	Ohio	Ohio	W. Va.	Pa.
Seam	#9	#6-A	Pgh. #8	Hernshaw	Pgh.
County	Belmont	Harrison	Jefferson	Kanawha	Washington
Type Mining	strip	deep	strip	deep	deep
Preparation	raw	raw	washed	washed	washed
Total Sulfur %	4.34	3.28	4.24	1.02	1.42
Pyritic Sulfur %	2.11	2.25	2.85	0.17	0.55
Determinations (ppm)	0.23	0.34	0.22	0.070	0.13
	0.15	0.36	0.24	0.06	0.15
	0.15	0.33	0.17	0.15	0.077
	0.18	0.67	0.32	0.094	0.085
	0.19	0.43	0.22	0.080	0.13
	0.14	0.37	0.20	0.12	0.075
	0.15	0.41	0.28	0.028	0.082
	0.22	0.63	0.22	0.031	0.14
Average (ppm)	0.18	0.44	0.23	0.079	0.11
Standard Deviation	0.035	0.13	0.047	0.042	0.023

Table 1. Cont.

Sample No.	G-1	P-1	P-2	P-3	P-4	P-5
State	Indiana	Ky./W.Va.	Mont.	Mont.	Colo.	Ariz.
Seam	Ind. #3	#9	Rosebud	Tebo/Weir	Nucla	Red
County	Clay	Muhlenberg	Rosebud	Henry	Montrose	Navajo
Mining Type						
Preparation	washed	raw	raw	wash/raw	raw	raw
Total Sulfur %	4.37	4.46	0.85	9.37	0.80	0.44
Pyritic Sulfur %	1.67	2.43	0.26	5.81	0.23	0.11
Determinations (ppm)	0.043	0.20	0.056	0.17	0.040	0.046
	0.036	0.20	0.054	0.20	0.034	0.041
	0.060	0.36	0.080	0.21	0.041	0.066
	0.060	0.26	0.073	0.22	0.043	0.035
	0.054	0.24	0.048	0.22	0.033	0.071
Average (ppm)	0.051	0.25	0.062	0.20	0.038	0.052
Standard Deviation	0.010	0.066	0.014	0.021	0.004	0.016

Sample No.	C16987	C16891	TVA1013	TVA1014	TVA1013	TVA1014	TVA1015
State	Ill.	Ill.	Ky.	Ky.	---	---	---
Seam	Herrin #6	Herrin #6					
Sample Type					fly ash	fly ash	fly ash
Preparation	raw	raw					
Total Sulfur %	3.46	4.45					
Pyritic Sulfur %	2.07	2.36					
Determinations (ppm)	0.071	0.13	0.20	0.17	0.20	0.21	0.16
	0.096	0.11	0.21	0.14	0.14	0.17	0.15
	0.21	0.14	0.17	0.20	0.15	0.25	0.17
	0.13	0.12	0.27	0.14	0.20	0.11	0.14
	0.17	0.10	0.17	0.13	0.14	0.14	0.13
Average (ppm)	0.13	0.12	0.20	0.16	0.17	0.17	0.15
Standard Deviation	0.056	0.016	0.041	0.029	0.031	0.051	0.016

With 500 mg samples the procedure has a sensitivity of approximately 0.02 ppm. Precision was undetermined due to the apparent lack of homogeneity of some samples. This is illustrated with the values obtained for sample DRB-B. This coal represents the highest mercury concentration of those coals investigated. Although it represents the finest mesh group (minus 60 mesh) specific analyses resulted in extremely high mercury concentrations. The large variation between determinations of this sample suggests a non-homogeneous distribution of the mercury in the coal.

A modification of this procedure utilizes a double amalgamation reaction and eliminates the liquid oxidizing solution. A schematic of the apparatus is shown in Figure 3. The procedure is a modification of the double amalgamation method developed by Suhr.[4] The horizontal resistance wound tube furnace containing separate furnaces for the coal combustion and both amalgams used by Suhr is replaced with a vertical quartz tube containing the quartz graphite crucible and both amalgams. An air or oxygen stream is maintained through the system during the whole procedure. During the subsequent steps requiring the firing of the coal, amalgam 1, and amalgam 2 the quartz tube tube is lowered stepwise positioning the single induction furnace at the desired location.

The method consists of firing the coal sample in the quartz graphite crucible and then lowering the quartz tube firing each successive amalgam respectively. The system is vented, bypassing the quartz absorption cell, until the last amalgam is fired. After firing the final amalgam the mercury is carried by the air stream through the quartz absorption cell located in the optical path of the spectrophotometer. The double amalgamation is used to ensure the complete removal of any interferences. When silver foil is used a sulfide coating forms on the silver resulting in a constantly decreasing sensitivity with each successive analysis. Gold foil works very well in the amalgamators. This system has the advantage that there is no blank determination required.

SUMMARY

A method was presented for the analysis of coal for mercury at naturally occurring levels. The procedure consists of firing the coal in an induction furnace, separating the mercury from other interfering gaseous by-products by collection in a strongly acidic oxidizing solution and on a silver or gold amalgamator, and then determining the mercury concentration by a cold vapor flameless atomic absorption method. A modification of this procedure to perform a direct double amalgamation is briefly described.

REFERENCES

1) W. R. Hatch, and W. L. Ott, Anal. Chem. 40, 2085 (1968).

2) G. W. Kalb, A. A. Newsletter 9(4), 84 (1970).

3) R. R. Ruch, H. J. Gluskoter, and E. J. Kennedy, Illinois Geological Survey, Environmental Geology Notes 43, 12 (1971).

4) N. Suhr (personal communication).

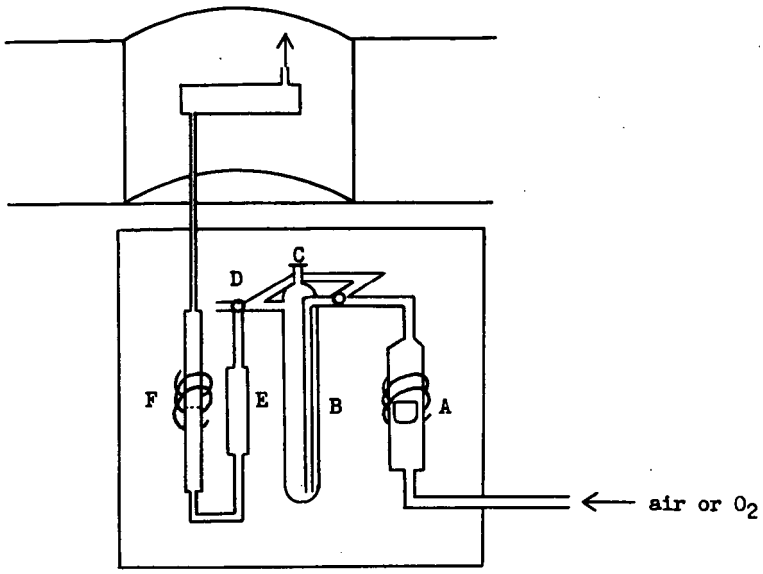

Figure 1. Schematic of mercury in coal apparatus.

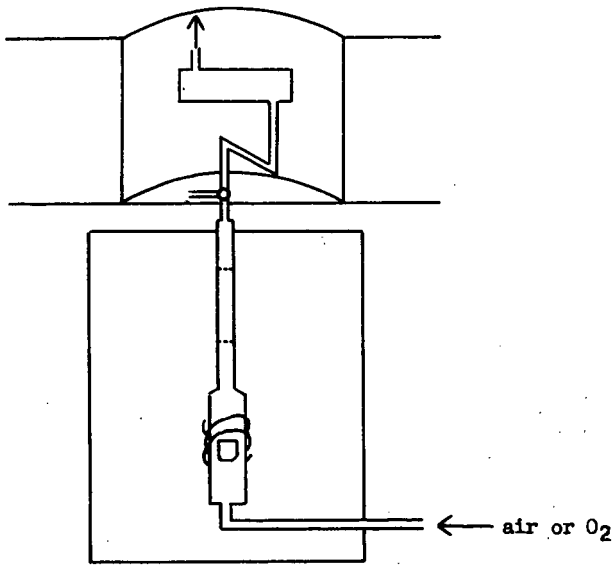

Figure 3. Schematic of modification for mercury in coal determinations by double amalgamation.

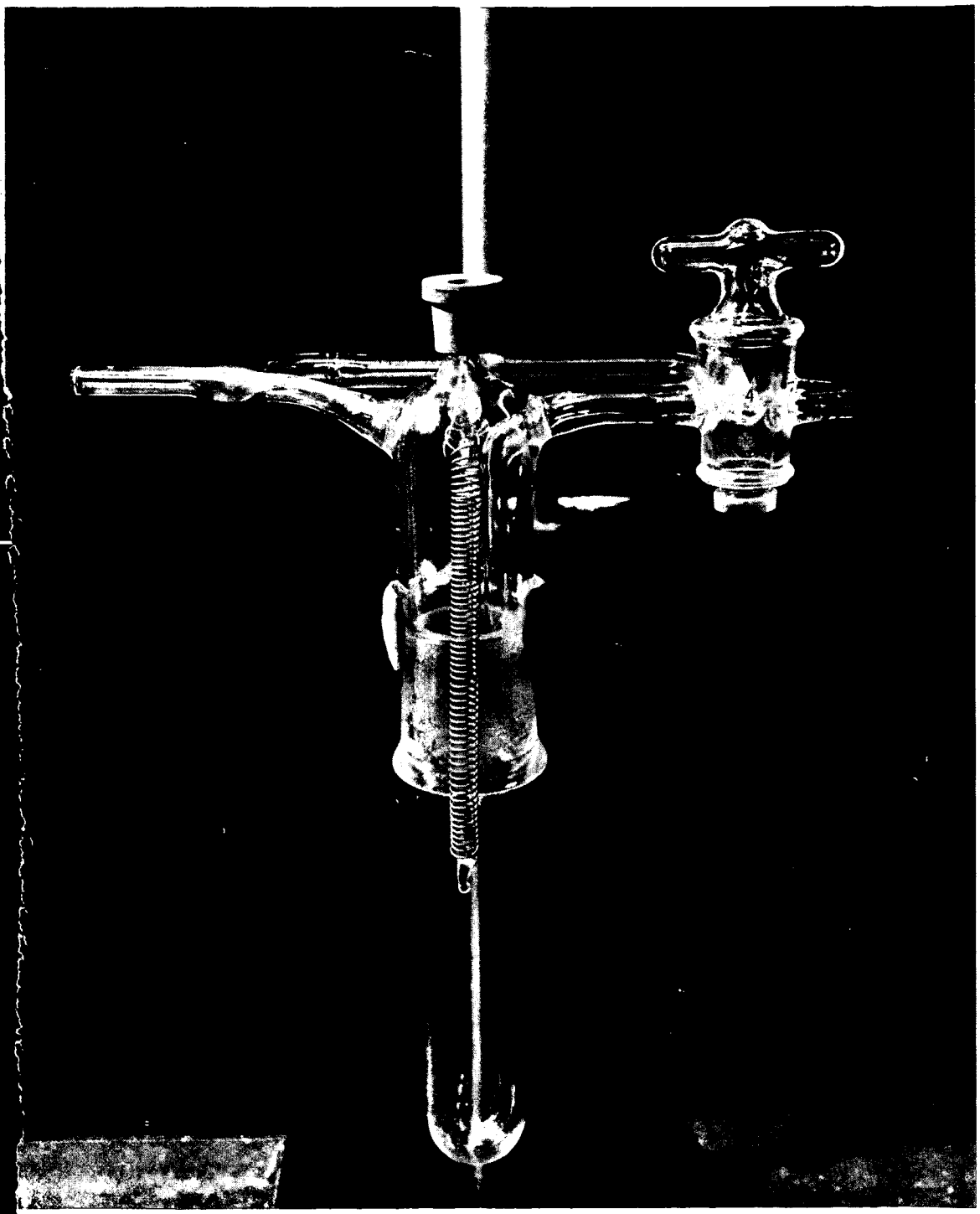

Figure 2.